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DIMENSIONAL STABILIZATION OF WOOD IN USE. (U)
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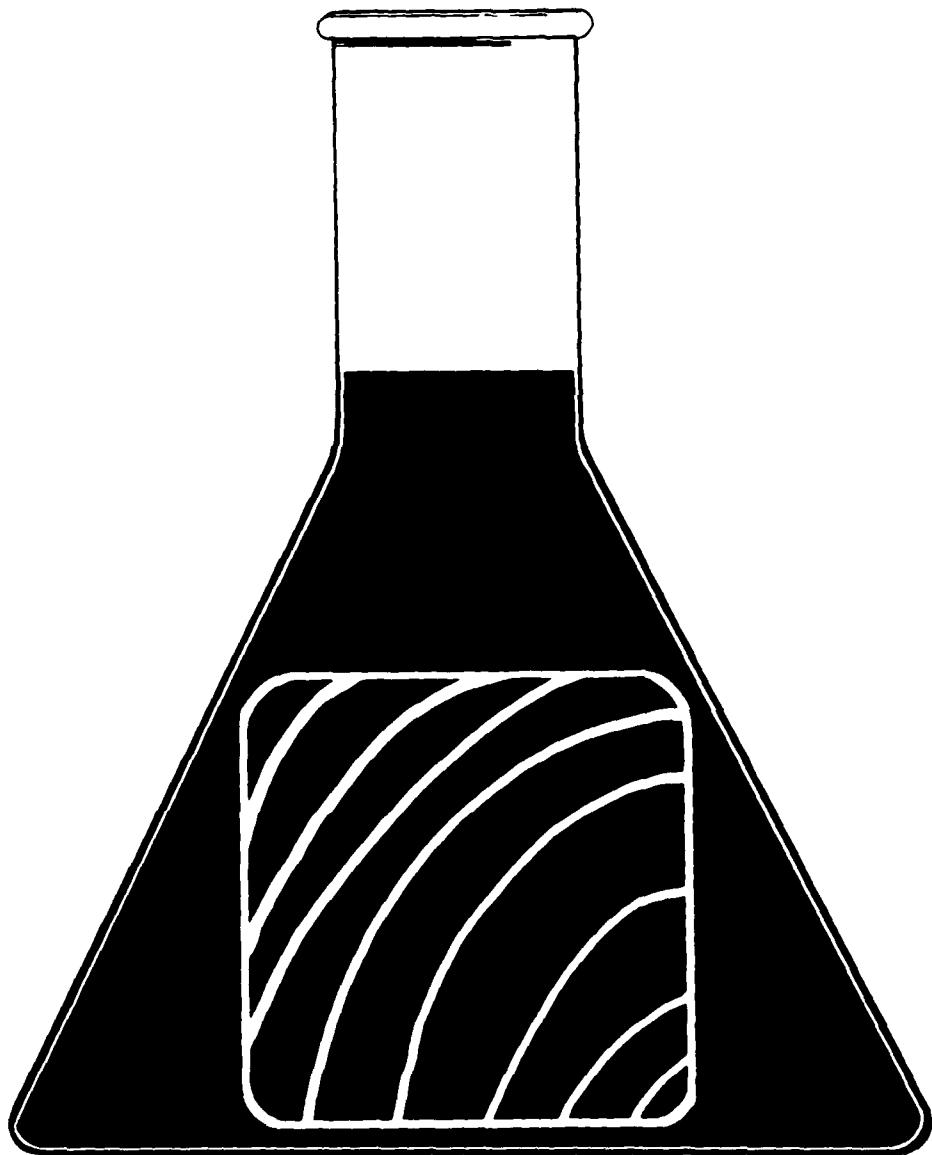
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Dimensional Stabilization of Wood in Use

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Abstract

Many techniques have been devised to reduce the tendency of wood to change dimensions in contact with moisture. *Treatments such as cross-lamination, water-resistant coatings, hygroscopicity reduction, crosslinking, and bulking are reviewed and recommendations for future research are given.*

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Dimensional Stabilization of Wood in Use

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Letter on File

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and
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INTRODUCTION

When moisture comes into contact with wood, the water molecules penetrate the cell wall and become bound to cell wall components through hydrogen bonding. With addition of water to the cell wall, wood volume increases nearly proportionally to the volume of water added. Swelling increases until the fiber saturation point has been reached. Water added beyond this point remains as free water in the lumen and does not cause further swelling. This process is reversible and accounts for the dimensional changes that occur when wood comes into contact with water vapor or liquid.

Though wood is one of the few natural products used throughout history with almost no modification of its properties, the tendency to change dimensions with changes in moisture content has caused problems with wood in use.

Background

In 1959 a seminar was held at the Forest Products Laboratory, Madison, Wis., on dimensional stabilization of cellulosic materials (18).² Conferees analyzed existing data and proposed new research programs to make wood products more dimensionally stable.

Six recommendations for future research were adopted: 1) That substantial additional basic information is necessary on wood-moisture relationships, microstructure of wood, and basic chemistry of wood; 2) That because the proper use of wood will minimize the limitations caused by lack of stability, the trade associations be encouraged to publicize the proper engineering principles of use; 3) That more economical means of mechanically stabilizing wood be further investigated, particularly with regard to composite structure, press drying to cause mechanical extension, and the use of other mechanical methods of distributing and minimizing the effect of dimensional changes; 4) That additional work be performed in connection with chemical stabilization. Because bulking and crosslinking appear to be the only chemical means of wood stabilization, newly developed chemicals should be screened. Fundamental studies of the extractives of wood should be undertaken to determine why some species are more stable than others; 5) That in the dimensional stabilization of paper a fundamental investigation of the effect of species be carried out; 6) That a bibliography be prepared which would serve as a reference for further research in the dimensional stabilization of wood.

Though a considerable amount of research has been conducted in the 21 years since the conference, if a seminar were held today on dimensional stability of cellulosic materials, the same six recommendations for future research would again be adopted along with perhaps two more.

Certainly one additional recommendation for research would be in the area of dimensional stability of reconstituted wood products such as fiberboard, particleboard, flakeboard, chipboard, and others.

Another recommendation would be in the area of dimensional stability of new and different wood species coming into the market. Very little research has been done in dimensional stability of tropical woods, mixed hardwoods, and second-growth softwoods in both solid and reconstituted wood products. Especially in the tropical woods the effects on dimensional stability of growth patterns, density, extractives, wax, and inorganic content need to be determined so that these resources can be utilized to their highest potential.

¹ Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

² This paper was presented, in part, at the International Union of Forestry Research Organizations, Division 5 Conference in Oxford, England, April 8-16, 1960.

³ Italicized numbers in parentheses refer to Literature Cited at the end of this report.

Characterization

A variety of terms is used to describe the degree of dimensional stability given to wood by various treatments: antishrink efficiency (ASE), swelling percent, dimensional stabilization efficiency, antiswelling efficiency, and percent reduction in swelling (R). Generally, they are calculated as:

$$S = \frac{V_2 - V_1}{V_1} \times 100 \quad (1)$$

where

S = volumetric swelling coefficient,
 V_2 = wood volume after humidity conditioning or wetting with water, and

V_1 = wood volume of oven-dried sample before conditioning or wetting,

then

$$R = \frac{S_2 - S_1}{S_1} \times 100 \quad (2)$$

where

R = reduction in swelling or antishrink efficiency (ASE) resulting from a treatment,

S_2 = treated volumetric swelling coefficient,

S_1 = untreated volumetric swelling coefficient.

There are many ways to classify treatments which result in dimensional stability of wood. Classification can be by treatment type, whether the treatment is by physical or chemical means, surface or penetrating, chemically bonded or nonbonded, or by method of treatment application. Stamm (30) used five classifications of methods to reduce swelling in wood and/or reduce the rate of water vapor or liquid uptake. They are: 1) Mechanical restraints by cross-laminating; 2) application of internal or external water resistant coatings; 3) reducing the tendency of wood to take on water (reduce hygroscopicity); 4) chemically crosslinking cell wall components of the wood; and 5) bulking the wood cell walls with chemicals.

Several reviews have been written which describe, in depth, each of these treatment types (20,21,26). A brief description of each type will be given here for comparison.

Treatment Types

Cross-Lamination

Wood swells in water 30 to 100 times more in the radial and tangential directions than in the longitudinal direction. Because of this, if wood veneers are glued perpendicular to one another, each ply is mechanically restrained from swelling. This has been used for years as the basis of product stability in plywood. Whether the cross-laminated structure is stable to water vapor or liquid uptake depends on the water stability of the glue joint. Plywood will swell in the thickness direction but is very stable in the two cross-ply longitudinal directions as long as the glue joint holds.

Water-Resistant Coatings

Water-repellent coatings can be applied either to the external surface of wood or to the internal surfaces (lumen walls). External and internal coatings reduce the rate of moisture uptake but, given enough time, moisture will penetrate all known coatings that will adhere to wood. The effectiveness of coating treatments are, therefore, not measured in terms of R or ASE values but rather in terms of moisture-excluding effectiveness (MEE), which is calculated as:

$$MEE = \frac{W_2 - W_1}{W_2} \times 100 \quad (3)$$

where

W_1 = weight gain in coated sample due to moisture pickup at 25°C, 97 percent relative humidity (RH) for 7 days,

W_2 = weight gain in uncoated control sample under the same conditions.

MEE values range from 99 percent for wood wrapped in aluminum foil sheets between coats of varnish, to 60 to 90 percent for two coats of pigmented oil-base paints over oil primer, to values of 50 to 85 percent for two coats of varnish or enamel. Penetrating oils and surface wax treatments give MEE values below 10 percent.

Impregnating wood with natural resins, waxes, or drying oils dissolved in a volatile solvent forms an internal coating on the lumen walls. Penetra-

tion is usually restricted to the outside 1/16 to 1/4 inch of the wood and does provide a degree of water repellency but does not impart any long-term dimensional stability. Water repellency is usually measured on ponderosa pine samples 1.5 by 0.25 by 8 inches (radial x tangential x longitudinal). The sample is preconditioned at 65 percent RH, dipped in a water-repellent solution for 10 seconds and again conditioned at 65 percent RH. The sample is then immersed in water and the tangential swelling that occurs in 30 minutes is measured on control and treated samples (1). The water repellency (WR) is determined as:

$$WR = \frac{T_1 - T_2}{T_1} \times 100 \quad (4)$$

where

T_1 = tangential swelling of control in 30 minutes of water soaking.

T_2 = tangential swelling of treated sample under same conditions.

Most values for WR range from 40 to 60 percent (1). Some of the tropical woods may have very high WR values because of high natural wax and extractive contents.

Another treatment that can be considered as an internal coating is the impregnation of nonswelling monomers which are then polymerized in the void structure of the wood. Because little or no wood swelling takes place upon treatment, very little of the polymerized chemical enters the cell wall. Treatment of wood with methyl methacrylate followed by heat or radiation polymerization is an example of a lumen fill or internal coating treatment (3). Polymer loadings over 100 weight percent gain (WPG) have been achieved. Because the lumen structure is filled, the rate of water uptake is greatly reduced. If the wood is exposed to water vapor or liquid long enough, swelling occurs to approximately the same extent as untreated wood. Some dimensional stability is achieved as R values up to 10 to 20 percent have been reported (4).

Hygroscopicity Reduction

As water hydrogen bonds to cell wall hydroxyl groups (which are available in all three major cell wall polymers—cellulose, hemicellulose,

and lignin) the cell wall expands to accommodate the water molecule. Any treatment that reduces the tendency of wood to take on water will result in a reduction in the tendency to swell.

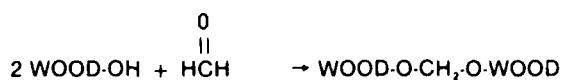
The optimum treatment would be to remove the hydroxyl groups on the cell wall polymers and thus remove the sites for hydrogen bonding to water. This is theoretically possible through reductive reactions; however, the wood would be destroyed by the treatments. The hydroxyl groups can act as reactive sites to bond chemicals that are hydrophobic (water repelling) and thus reduce the tendency to attract and bond to water. Chemical reactions with cell wall hydroxyl groups bulk the cell wall with bonded chemicals. This type of treatment will be discussed later under bulking treatments.

One example of a method to reduce the hygroscopicity of wood is heat treatment. Heating wood in the absence of oxygen to temperatures up to 350°C for a short time results in a 40 percent reduction in swelling (R or ASE = 40 percent) (11,22). Lower temperatures for longer periods of time produce the same results. The mechanism for imparting a reduction in hygroscopicity is thought to be due to thermal degradation of the hemicellulose component of the cell wall (15). This component, the most susceptible to thermal degradation, is the most hygroscopic of the cell wall polymers. Its degradation products polymerize under heat to produce a water-insoluble polymer.

A heat treatment which results in R or ASE = 40 (for example, 280°C for 10 min) also results in a 90 percent reduction in abrasion resistance, 40 percent loss in toughness, 20 percent loss in hardness, and a 17 percent loss in modulus of rupture (22). Loss of these strength properties is the primary reason heat treatments have not been utilized to any great extent by industry.

Crosslinking

If structural units of the wood cell wall are chemically bound together (crosslinked), the bonds restrain the units from swelling when moisture is present. One of the most widely studied chemical systems for crosslinking is the reaction between wood cell wall hydroxyls and formaldehyde:



Crosslinking can take place between hydroxyl groups on the same or different cellulose, hemicellulose, and lignin polymers. The reaction is usually catalyzed with strong acids. A WPG of 3.1 percent results in an R or ASE = 47 percent; at 5.5 WPG, R = 60 percent; and at 7 WPG, R = 90 percent (17,27).

The mechanical properties of formaldehyde-treated wood are all reduced from those of untreated wood. Toughness and abrasion resistance are greatly reduced (17,27). Crushing strength and bending strength are reduced about 20 percent and impact bending strength is reduced as much as 50 percent (2). Most of the loss in wood strength properties is probably due to structural cellulose units being hydrolyzed by the strong acid catalyst.

A definite embrittlement is observed in formaldehyde-treated wood. This embrittlement may be due to the short inflexible crosslinking unit of the -O-C-O- type. If the inner carbon unit were longer, there would be more flexibility in this unit and the embrittlement should be reduced. While increased flexibility might reduce embrittlement, it would also reduce the dimensional stability by allowing structural units to expand more upon wetting. It would be interesting to use reactive difunctional chemicals with longer carbon chains to achieve crosslinking. For example, difunctional epoxides or isocyanates of 4 to 10 carbon atoms reacted under mild conditions might achieve the desired dimensional stability through crosslinking without the accompanying loss of mechanical properties or embrittlement.

It may also be possible to crosslink surface structural units between different wood particles in reconstituted wood products and increase the dimensional stability of such products as fiber-, chip-, flake-, and particle-boards. If the reaction took place during the heat/compression stage in the board process, the particles might be close enough for crosslinking between particles to take place.

Bulking Treatments

By far the greatest amount of research for dimensional stability of wood has been carried out in the area of cell wall bulking treatments. It has been shown that the increase in wood volume upon treatment is directly proportional to the theoretical volume of chemical added (6). The volume of wood increases with increasing chemical added to about 25 WPG at which point the treated volume is approximately equal to green volume (9). When this bulked wood comes into contact with water, very little additional swelling can take place. This is the mechanism for the effectiveness of bulking treatments on dimensional stability.

Bulking treatments can be divided into three classes: nonbonded and water leachable; nonbonded and water nonleachable; and bonded and water nonleachable.

Nonbonded-Leachable.—The wood cell wall can be bulked with concentrated solutions of salts or sugars. Solutions of manganese, sodium, barium, magnesium, and lithium chloride and solutions of sucrose, glucose, and fructose have been used to reduce the swelling of wood (13,21). These chemicals make the wood even more hygroscopic, so the wood is usually finished with two coats of varnish to seal the chemical in the wood. These chemicals are also very soluble in water and are easily leached if the treated wood comes into contact with water.

Another nonbonded-leachable treatment utilizes polyethylene glycol (PEG) (16,19). In this case the wood is usually treated in a green condition and the PEG is exchanged for the cell wall water. The treatment most often used is a 30 percent by weight solution of PEG-1000. The green wood is soaked in this solution for a length of time depending upon the thickness of the sample. This treatment is also hygroscopic and two coats of polyurethane varnish are usually applied to help seal in the PEG and help seal out water. Maximum $R \approx 80$ percent is achieved at PEG loadings of

45 WPG. The strength properties of PEG-treated wood approximate those of untreated green wood.

Nonbonded-Nonleachable.—Treatment of wood with aqueous solutions of phenol-formaldehyde resin-forming compounds gives a bulked product where the chemicals are not attached or bonded to the cell wall components but form insoluble polymers which will not leach out in water. Usually thin veneers are treated to 25 to 35 percent resin-forming materials on the basis of the weight of dry untreated wood. After uniform diffusion of the resinoids into the cell wall structure, the wood is partially dried and the resin is then cured at about 150° C for 30 minutes (24). The resulting cured product, commonly termed "impreg," can then be laminated with practically all kinds of adhesives; however, water-insoluble types are usually used. Thin veneers are treated because the treating time varies directly to the square of the thickness. Green veneer, 1/32 inch thick, can be treated by soaking 1 to 2 hours, whereas green veneer, 1/8 inch thick, will require about a day. At weight gains of 25 to 40 percent resin, the treated impreg will have an $R = 60\text{-}70$ percent (24). Impreg has been used for electrical equipment because of its improved electrical properties, for acid tanks because of its high acid resistance, and for pattern wood dies because of its dimensional stability (12).

When phenol-resin-treated wood is highly compressed before curing of the resin, a product commonly known as "compreg" is made. Compreg with a specific gravity of 1.3-1.4 containing 30 percent water-soluble phenol-formaldehyde resin is achieved by applying pressures of 1,000 to 1,200 psi and a temperature of 150° C (10,25).

In a 24-hour water soaking dimensional stability test, compreg has an $R \approx 95$ percent. The rate of water pickup is so slow that complete swelling equilibrium of a 1/2-inch sample is not complete in a year at room temperature (14). For this reason, results from short-term low-temperature water-soaking test data have little meaning for compreg.

One interesting nonbonded-nonleachable treatment (23) that has received little recent attention is replacing cell wall water with waxes. In a two-phase process, water can be removed from a thin green sample by boiling the sample in an organic sol-

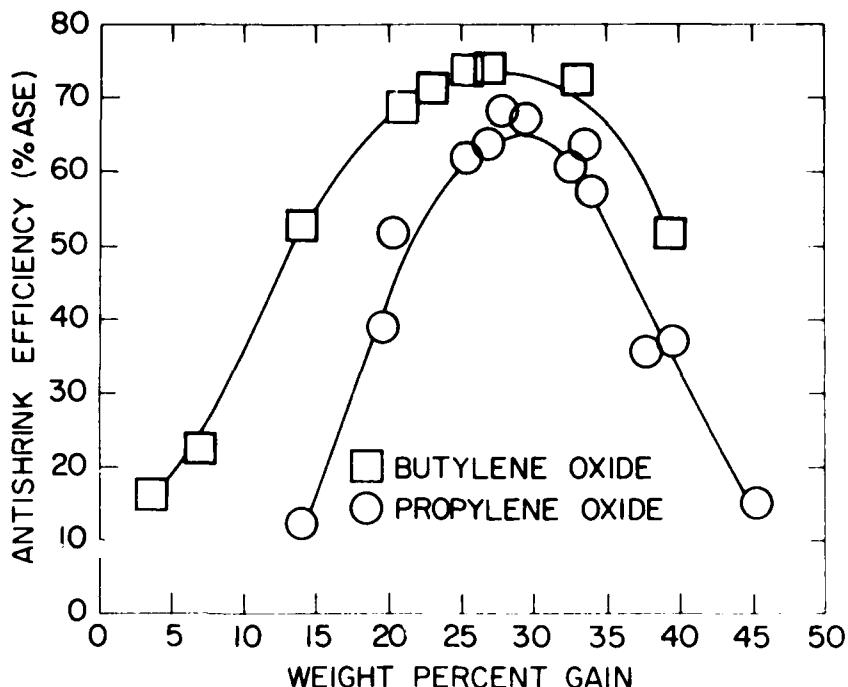


Figure 1.—With epoxide treatment, antishrink efficiency falls off beyond about 33 weight percent gain, the point where cell wall rupturing begins.

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vent with a boiling point higher than that of water. Ethylene glycol monoethyl ether (Cellosolve) has a boiling point of 135° C and is soluble in water. The water in the wood is replaced by the glycol with little wood swelling. The glycol in the wood can then be replaced by a molten wax whose melting or boiling point is higher than the boiling point of Cellosolve. The wax is not able, because of its molecular size, to replace all of the potential sites where water can interact with the cell wall polymers but it is possible to replace up to 80 percent of the original bound water with wax (23). Part of the wax ends up in the lumen structure, so much more wax is used than just that needed to replace cell wall water. Reductions in swelling of as much as 80 percent have been achieved. However, because the process is used with thin veneers and it interferes with gluing and finishing, commercialization of the procedure has not been undertaken. Most of the early research was done with common beeswax and it would be interesting to reinvestigate this procedure now with some of the modern specialty waxes.

Bonded-Nonleachable.—Through chemical reactions it is possible to add an organic chemical to the hydroxyl groups on wood cell wall components. This type of treatment reduces the hygroscopicity of the wood as described earlier and also bulks the cell wall with a permanently bonded chemical.

In a recent paper, the advantages and disadvantages of bonding chemicals to wood were reviewed (5). Many reactive chemicals have been used to chemically modify wood. For best results chemicals used should be capable of reacting with wood hydroxyls under neutral or mildly alkaline conditions at temperatures below 120° C. The chemical system should be simple and must be capable of swelling the wood structure to facilitate penetration. The complete molecule must react quickly with wood components yielding stable chemical bonds and the treated wood must still possess the desirable properties of untreated wood.

Chemicals such as anhydrides, epoxides, and isocyanates all give R or $ASE = 70\text{-}75$ percent at $WPG \approx 20\text{-}30$. In all of these treatments, as

the chemical add-on increases, the R or ASE increases (fig. 1). In the case of epoxy and isocyanate reactions above about 35 WPG, the R or ASE

starts to drop (7,9). Above this WPG the volume of added chemical becomes great enough to rupture the cell wall. Electron micrographs of

wood clearly show the splits in the cell wall at high chemical loadings (fig. 2). The isocyanates and epoxides react and swell the cell wall and con-

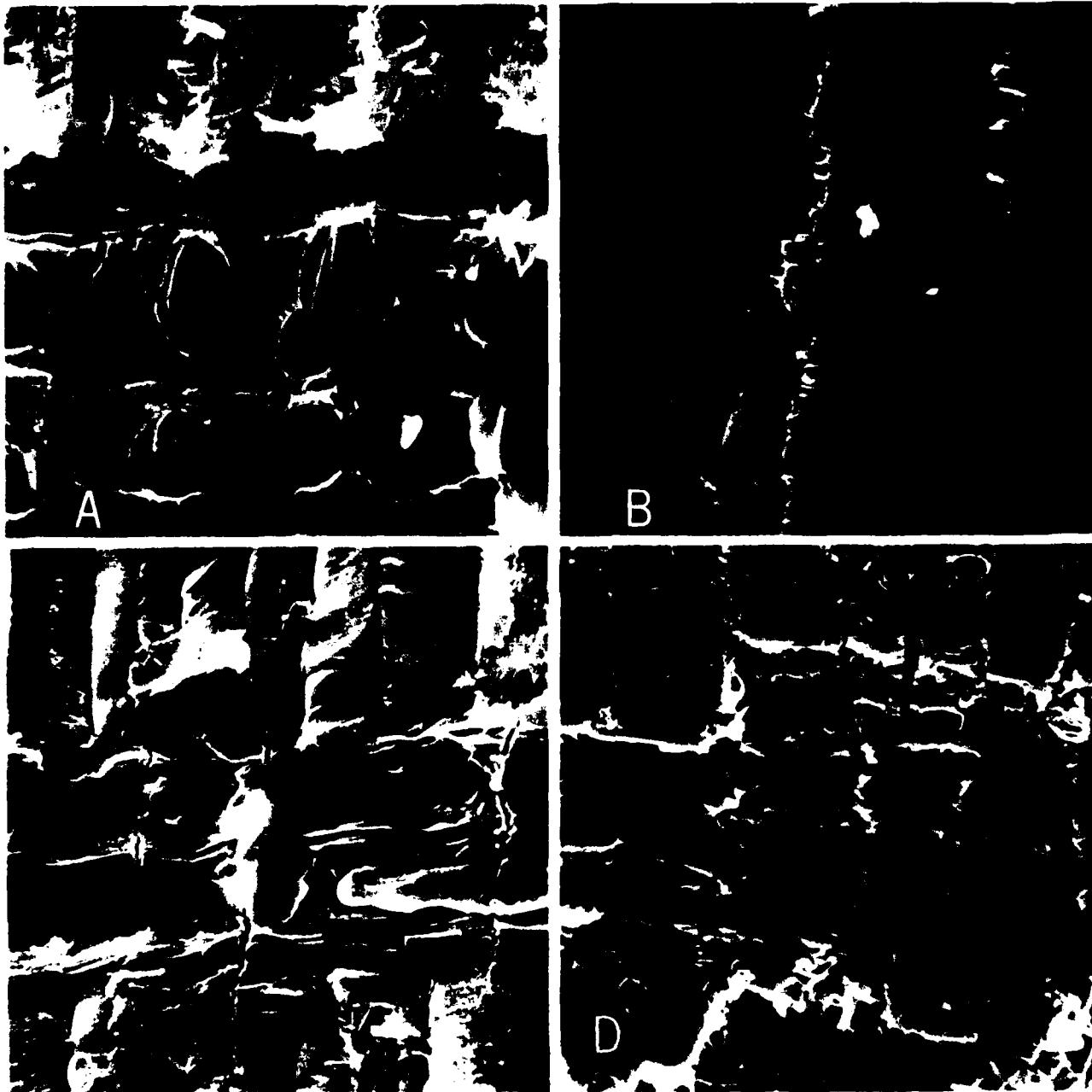


Figure 2. Scanning electron micrographs of radial split southern pine, showing swelling of wood when treated with propylene oxide triethylamine. No swelling is shown in (A), the untreated control (1:100X). In (B), wood is treated to green volume (1:100X). In (C), wood is superswollen above green volume at 32.6 WPG and cell wall rupture is apparent (600X). In (D), rupture is pronounced at 45.3 WPG (550X).

tinute to do so until the cell wall must rupture to accommodate more reacting chemical. Water can then interact with newly exposed ruptured cell wall component hydroxyl groups causing the wood to superswell above green volume.

The maximum of 70 to 75 percent dimensional stability is due to the size and hydrophilic nature of the reacted chemicals. To access all sites that water could bond to, the reacting chemical would have to penetrate as well as water does and be the same molecular size or smaller. None of the chemicals used so far penetrate as well, or as completely, as water. Because the hydroxyl oxygen is not removed during the reaction, there is still an oxygen atom available to hydrogen bond to water. For these reasons, it is not possible for chemical modification of wood treatments to achieve 100 percent dimensional stability.

Conclusions

There are two basic types of wood treatments for dimensional stability: 1) those which reduce the rate of water vapor or liquid absorption but do not reduce the extent of swelling to any great degree and 2) those which reduce the extent of swelling and may or may not reduce the rate of water absorption (fig. 3). Terms most often used to describe the effectiveness of the first type of treatment are moisture-excluding effectiveness (MEE), which can be determined in either water or water vapor form, and water repellency (WR), which is a specific liquid test. The term used to describe the effectiveness of the second type of treatment is reduction in swelling (R) or antishrink efficiency (ASE). Most of the type (1) treatments have very low R or ASE values. The R or ASE values can be determined in water vapor tests or single-soak liquid test for water-leachable treatments, or in double-soak liquid tests for nonleachable treatments.

In selecting a treatment to achieve product stability to moisture, at least three factors must be considered. The environment of the end product is the most important factor. If the product will come into contact with water, nonleachable—and perhaps even bonded—treatments will be needed. If, however, the product will be subjected to changes in relative humidity in an indoor environment, a leachable

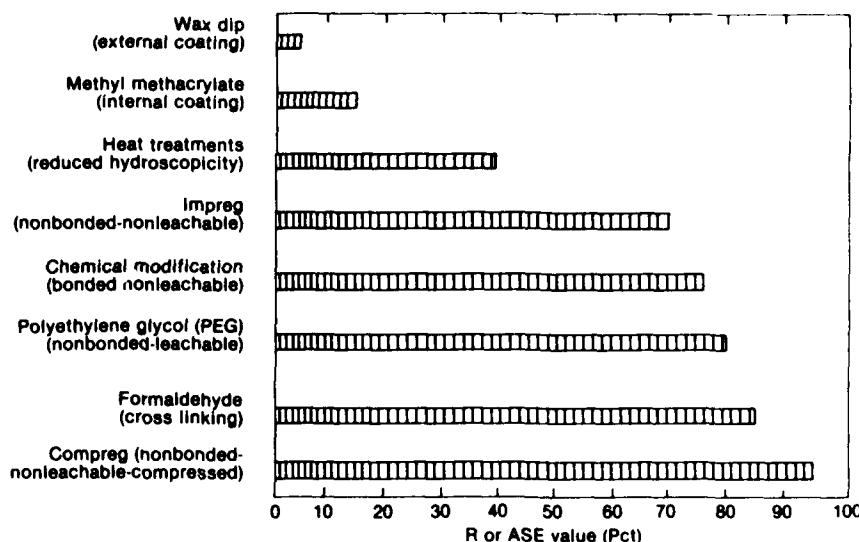


Figure 3.—Comparison of wood treatments and the degree of dimensional stability achieved.

or water-repellent treatment might be satisfactory. The degree of dimensional stability must also be considered. If very rigid tolerances are required in a product—as in pattern wood dies—a treatment with very high R or ASE values is needed. If, on the other hand, only a moderate degree of dimensional stability is satisfactory, a less rigorous treatment will suffice. A final consideration is the cost effectiveness of a treatment. For example, the millwork industry uses a simple wax dip treatment to achieve a moderate degree of water repellency. They would, no doubt, like a higher degree of water repellency or dimensional stability but the cost to achieve this may not be recoverable in the marketplace. On the other hand, musical instrument makers require a very high degree of dimensional stability and the value of the final instrument can absorb the high cost to accomplish the desired results.

Recommendations for Future Research

Six recommendations for future research in wood stabilization were made at the 1959 conference on dimensional stability. Two more recommendations have been added to this list. These eight recommenda-

tions are very general and pertain to broad research areas. Many specific research problems need further investigation. For example, the properties of coatings can be tailored to perform more duties than just water repellency. A water-repellent coating could also serve as an ultraviolet screen or flameproofing shield. It could also contain bound functional insecticides or fungicides that could protect the wood from attack by insects and decay organisms.

In bonded bulking treatments, the bound chemical could be a fire retardant if the bonded chemical has an adequate distribution in the wood structure, the treated wood is not only dimensionally stabilized but resistant to attack by termites, decay organisms, and marine organisms (5). Chemical modification of wood could provide a variety of nonleachable treated wood products that are both dimensionally stabilized and fire retardant or nonbiodegradable or acid and base resistant and so on.

Complete dimensional stability of wood (R or $ASE = 100$) has never been achieved, and perhaps never will be, but there is much to learn in the study of wood:moisture relationships.

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